BIOMARKERS FOR ANALYSIS OF MARTIAN SAMPLES.

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A central problem in organic analyses of Martian samples (*in situ* or returned) is not only identifying and quantifying organic compounds that may be present, but also distinguishing those molecules produced abiotically from those synthesized by extinct or extant life. Terrestrial biology uses only a limited number of the large variety of organic compounds that can be synthesized abiotically under plausible cosmochemical conditions, and would have thus possibly been available at the time of the origin of life. The detection on Mars of a small subset of these possible prebiotic compounds would be suggestive, but not compelling, evidence of past or present Martian biochemistry. The most reliable indicator of the biological vs. abiotic origin of organic molecules is molecular homochirality (1). The structural principles on which biomolecular activity is based lead us to believe that any functional biochemistry must use a single optical isomer, or enantiomer, of any optically active molecule. Proteins, for example, cannot fold into bioactive configurations such as the α-helix if the amino acids of which they are composed are racemic (i.e., consist of equal amounts of D- and L-enantiomers). In contrast, all known laboratory abiotic synthetic processes result in racemic mixtures of chiral amino acids, and the amino acids in carbonaceous chondrites are almost entirely racemic (2). Therefore an enantiomeric selection process would be required at some stage in the origin or evolution of life. Because there is no apparent biochemical reason why L-amino acids would be selected over D-amino acids, the selection of L-amino acid homochirality on Earth has been considered to be simply a matter of chance.

Of the homochiral compounds used in terrestrial biochemistry, amino acids are the most suitable for use as biomarkers in extraterrestrial samples. Amino acids are in general less prone to decomposition than other chiral compounds such as ribose and deoxyribose. Detection techniques with sub-pmol sensitivities exist for amino acids, and are potentially adaptable for use on Mars lander or rover spacecraft (3). Although we do not know whether amino acids were a component of the first self-replicating systems, or even required for the origin of life, a biochemical system of any significant complexity would probably evolve protein catalysis at an early stage. The detection of a non-racemic mixture of indigenous amino acids in a Martian sample would be strong evidence for the presence of an extinct or extant biota on Mars. The finding of an excess of D-amino acids would provide irrefutable evidence of unique Martian life that could not have been derived from seeding the planet with terrestrial life. In contrast, the presence of amino acids with D/L close to 1.0, along with abiotic amino acids such as α-aminoisobutyric acid (Aib), would be indicative of an abiotic origin, although we have to consider the possibility that the racemic amino acids were generated from the racemization of biotically produced amino acids (4).

We have used chiral amino acid analyses to investigate possible terrestrial organic contamination of the Antarctic shergottite EETA79001 (5). This meteorite contains several hundred ppm low-temperature combustible carbon, which has been suggested to be endogenous martian organic material (6). Analyses of a small fragment of the EETA79001 carbonate material detected only the L-enantiomers of the amino acids found in proteins. There is no indication of the presence of Aib, which is a common amino acid in carbonaceous meteorites and is readily synthesized in laboratory-based prebiotic experiments. However, Aib is not one of the amino acids normally found in the proteins of terrestrial organisms (7). The amino acids in this Martian meteorite are thus most likely terrestrial contaminants concentrated by sublimation of Antarctic ice and introduced into the meteorite by meltwater which percolated through the meteorite.

In addition, we have examined PAHs in the EETA79001 carbonate and basaltic matrix material, as well as several Antarctic carbonaceous chondrites (8), using laser desorption/ionization mass spectrometry (LDMS). A similar technique was used by McKay et. al. (9) for the detection of PAHs in the ALH84001 meteorite. We found that many of the same PAHs detected in the ALH84001 carbonate globules are present in Antarctic carbonaceous chondrites and in both the matrix and carbonate (druse) component of EETA79001. We also investigated PAHs in Antarctic Allan Hills ice and found that carbonate is an effective scavenger of PAHs in ice meltwater, and the distribution of PAHs extracted

from the ice is similar to that found in both Martian meteorites.

An important issue to consider is whether PAHs are useful "biomarkers" in the search for extinct or extant life on Mars. PAHs are ubiquitous on the Earth, derived by both the combustion of biomass and fossil fuels, and the slow geochemical aromatization (millions of years) of sterols and triterpenes present in many organisms (10, 11). This aromatization process can be accelerated by hydrothermal activity (12), and thus can occur over a much shorter geological time scale (thousands of years). PAH tracers of combustion have been identified in Greenland ice (13, 14). PAHs are also widespread in the cosmos (15) and are commonly found in carbonaceous chondrites (16) and interplanetary dust particles (17). McKay et al. (9) argue that the simple distribution of PAHs found in the ALH84001 is unique and different from that observed in terrestrial samples and carbonaceous chondrites, and thus, the observed PAHs provide evidence of extant or extinct life on Mars. In fact, we have observed similar distributions of PAHs in hydrothermal vent sediments and Antarctic carbonaceous chondrites.

On the Earth, PAHs do not play a major role in the biochemistry of any known organism. Moreover, with the possible exception of obtaining the stable carbon and hydrogen isotopic compositions for these compounds, the molecular architecture of PAHs cannot be used to distinguish between abiotic and biotic processes. Thus, whether the PAHs detected in ALH84001 are diagenetic products of biologically derived compounds or are abiotic in origin is difficult, if not impossible, to establish.

In contrast to PAHs, amino acids play a major role in biochemistry on the Earth today and amino acid homochirality provides a reliable way of distinguishing between abiotic and biotic origins (3). As has been discussed above, abiotic synthetic processes yield racemic mixtures of amino acids while terrestrial organisms use L-amino acids for protein biosynthesis. Thus, amino acids may be the biomarker of choice in any search for past or present life on the surface of Mars. Future missions to Mars may provide us with a unique opportunity to test for these compounds in situ, and sample return missions will provide the pristine samples needed to conclusively evaluate the question of life on Mars.

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